

METHOD FOR PROCESSING SULFIDE MINERALS AND CONCENTRATES.

The method is referred to hydrometallurgical process and serves for recovery of nonferrous, rare and precious metals from sulfide minerals and concentrates.

The practice of sulfide ores processing is based on the fact that essential amounts of nonferrous, rare and precious metals are constituents of the sulfide mineral structure and cannot be extracted without oxidation of the sulfides. Rich ores are processed by direct oxidation, while gravity- and flotation concentrates are usually obtained from poor ores, major amount of sulfide minerals transferring to the concentrates.

The known methods for oxidation of sulfide ores and concentrates, like roasting, pressurized autoclave oxidation, nitric acid oxidation, bacterial oxidation, etc. have significant shortcomings, which hamper their extensive use in current industrial practice.

The known method of hydrometallurgical recovery of metals from ores, which is described in PCT application No. 94/17216, Int. Cl.: C22B 3/44, 3/06, 3/08, 3/00, 15/00, Publication Date 4.08.1994, has much in common with the invention proposed and consists in oxidation of sulfide minerals by nitric acid. Oxidation of sulfide minerals with concentrated nitric acid gives rise to nitric acid thermal decomposition effect catalyzed by transition metal cations transferred into

solution from the concentrate. It results in the necessity to spend 3-6 weight amounts of acid of theoretically required one, which makes the oxidation unfit for economic reasons. Besides, after the concentrates oxidation with nitric acid the solution contains a great amount of nitrates, which impedes their safe discharge to the environment.

There are well-known processes reducing consumption of nitric acid for concentrates oxidation due to feed of pure oxygen to the oxidation reactor to convert nitrogen oxides into regenerated nitric acid directly in the reactor. One of the processes is described in the PCT application No. 97/11202, Int. Cl.: C22B 3/06, 11/00, Publication Date: 27.03.97. However, the processes due to thermodynamic reasons involve oxidation of a portion of sulfide sulfur to elementary sulfur, which shields the surface of gold and other precious metals and deteriorates their further recovery.

One feature in common between the Prior Art and technical approach proposed consists in the stage of sulfide mineral oxidation by nitric acid. The action of nitric acid brings about transfer of metal into solution, which facilitates its recovery.

The technical approach proposed describes the process, which permits:

1. Oxidation of sulfide minerals contained in ores and concentrates for subsequent, as complete as practicable, recovery of nonferrous, rare and precious metals (using the well-known techniques),
2. Oxidation of sulfide minerals that occurs under conditions ruling out formation of elementary sulfur with simultaneous hydrolysis of trivalent iron into compounds binding arsenic into water-insoluble form,
3. Using nitrogen oxides as a catalyst of sulfides oxidation, moreover, the regeneration of nitrogen oxides from lower valence forms into higher ones is realized using either air or oxygen,

4. Using nitrogen compounds, which are catalysts of sulfide oxidation, in the most active form, i.e. as nitrous acid and its oxides.

The invention is aimed at creating conditions for the most complete extraction of metals, preventing formation of elementary sulfur.

The objective is attained by means of the following: the hydrometallurgical method of sulfide minerals and concentrates processing, which involves sulfide minerals oxidation in aqueous medium using nitrogen oxides, envisages that the sulfide materials containing slurry are subjected to oxidation of the sulfide and the oxidation is realized under controlled conditions of the slurry acidity, i.e. with constant neutralization of sulfuric acid formed as a result of the sulfides oxidation, moreover, sulfuric acid is neutralized to acidity level, at which no formation of elementary sulfur occurs, while natural or artificial substances, such as CaCO_3 , MgCO_3 , Ca(OH)_2 , CaO , NaOH , CaHPO_4 etc., are used as acidity neutralizers; the choice of a specific neutralizer is dictated by the necessity of formation of slurry neutralization products with assigned physicochemical properties: filterability, slurry thickening, arsenic substance insolubility, non-toxicity and other required properties. Oxidation of sulfide minerals is realized under agitation providing sufficient mass exchange and efficient occurrence of chemical reactions. Oxidation is realized in the temperature range of 20-90°C, mainly in the range of 65-85°C. The required temperature is maintained by removal of heat released during sulfides oxidation from the oxidation reactors. The liquid-to-solid ratio may vary from 1:1 to 5:1, depending on the effectiveness of the required precipitate formation and proceeding of sulfide oxidation reactions. Nitric and nitrous acids, as well as their oxides, mainly nitrous acid, HNO_2 , and its oxide, N_2O_3 , are used as oxidizing agents in this patent application. Air or oxygen is used for regeneration of nitrogen oxides from NO to N_2O_3 . Absorption of nitrogen oxides for their separation from the air inert nitrogen is realized by sulfuric acid solutions, their prevailing concentration 75-98%. Sulfuric acid denitration is realized both thermally by heating mainly to a temperature not

exceeding 250°C, and chemically, i.e. by introduction of denitrating substances, like alcohols, formaldehyde and other chemical reducing agents. Absorption of nitrogen oxides for their separation from inert nitrogen in the air is realized in agreement, using monovalent copper salt solutions. Denitration of the monovalent copper salt solutions is realized by dosed supply of compressed air, possibly with simultaneous heating of the solution. Monovalent copper solutions may contain stabilizing agents impeding copper oxidation from monovalent to bivalent one, as bivalent copper solutions are not effective solvents of NO. The well-known substances, namely tributyl phosphate and adipodinitrile, as well as reducing agents like formaldehyde, hydrazine, etc. can be used as stabilizing agents. Nitrogen oxide regeneration process involving NO oxidation by pure oxygen is realized at a temperature of 15-25°C in individual regeneration oxidizer, which permits converting NO into N_2O_3 and preventing nitric acid accumulation in the slurry.

The flowsheets illustrated in Fig. 1-3 are provided for clarifying the essence of the technical approach proposed. The flowsheet in Fig. 1 depicts schematically the hardware for oxidation of sulfide ores and concentrates with nitrogen oxides regeneration by air and absorption by sulfuric acid, where:

- 1 – sulfide ores and concentrates oxidation reactor
- 2 – blower
- 3 – oxidizer
- 4 – absorber
- 5 – denitrator
- 6 – pump
- 7 – fan.

Flowsheet in Fig.2 depicts schematically the hardware for oxidation of sulfide ores and concentrates with absorption of nitric oxide by copper salts and regeneration with air, where:

- 1 – sulfide ores and concentrates oxidation reactor

- 2 – blower
- 3 – oxidizer
- 4 – absorber
- 5 – denitrator
- 6 – pump
- 7 – fan.

Flowsheet in Fig.3 depicts schematically the hardware for oxidation of sulfide ores and concentrates with regeneration of nitrogen oxides with oxygen, where:

- 1 – sulfide ores and concentrates oxidation reactor
- 3 – oxidizer
- 6 – pump.

Description of the technological process:

The schematic hardware block diagram for oxidation of sulfide ores and concentrates with nitrogen oxides regeneration by air and absorption by sulfuric acid is provided in Fig. 1. Oxidation of sulfide minerals takes place in reactor 1 equipped with a slurry stirring device. Gases from the reactor top section, consisting primarily of NO, enter oxidizer 3, to which from blower 2 via regulator the air enters in the amount necessary for NO oxidation to N_2O_3 . Downstream of the oxidizer nitrous gases enter absorber 4, where nitrous gas is absorbed by sulfuric acid solution, after that nitrogen via fan 7 is released to the atmosphere, while sulfuric acid saturated with nitrous gases enters denitrator 5. In the denitrator as a result of heating and interaction with special chemical additions sulfuric acid evolves nitrous gases, absorbed by the acid in the absorber, into gaseous phase, and then the gases enter the sulfides oxidation reactor. After denitration sulfuric acid is fed by pump 6 to absorber 4 for continuing the nitrous gases absorption.

The schematic hardware block diagram for oxidation of sulfide ores and concentrates with absorption of nitric oxide by copper salts and regeneration with air is provided in Fig. 2. Oxidation of sulfide minerals takes place in reactor 1 equipped with a slurry stirring device. Gases from the reactor top section, consisting primarily of NO, enter absorber 4, where nitric oxide, NO, is absorbed by copper salt solution, after that nitrogen via fan 7 is released to the atmosphere, while copper salt solution saturated with nitric oxide, enters denitrator 5. In the denitrator as a result of NO oxidation and interaction with special chemical additions copper salt solution evolves into gaseous phase nitrogen oxide, NO, absorbed in the absorber, which enters oxidizer 3, to which air is fed from blower 2 via a regulator in the amount necessary for NO oxidation to N_2O_3 . From oxidizer 3 nitrous gases enter the sulfides oxidation reactor.

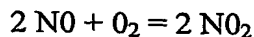
The schematic hardware block diagram for oxidation of sulfide ores and concentrates with regeneration of nitrogen oxides by oxygen is provided in Fig. 3. Oxidation of sulfide minerals takes place in reactor 1 equipped with a slurry stirring device. Gases from the reactor top section, consisting primarily of NO, enter oxidizer 3, to which pure oxygen is fed in the amount necessary for N_2O_3 formation. Regenerated nitrogen oxides are fed by pump 6 to the sulfides oxidation reactor.

Oxidation of sulfide ores and concentrates is realized with observing and controlling the following conditions:

1. The slurry acidity is controlled so that the concentration of free sulfuric acid formed during sulfide sulfur oxidation is not in excess of 10-20 g/l of the slurry. It is achieved by introducing substances, which neutralize acidity, into the slurry. $CaCO_3$, $MgCO_3$, CaO , $Ca(OH)_2$, $CaHPO_4$, $NaOH$ and other natural or artificial acidity neutralizers can be among the substances mentioned. When choosing a specific neutralizer, one should bear in mind the necessity to form precipitates, i.e. products of the slurry neutralization and trivalent iron hydration, featuring the assigned properties: thickening ability, filterability, insolubility of

arsenic, antimony compounds, and other toxic substances contained in precipitates. The above-mentioned conditions permit oxidizing all sulfide sulfur to sulfate one without formation of the elementary form. Simultaneously arsenic, antimony and other toxic elements for the process and the environment are transferred to water-insoluble state.

2. The process of oxidation in the reactor is arranged so that nitrous acid, HNO_2 , and its oxide, N_2O_3 , are oxidizing agents, while the air oxygen is used for the acid and its oxide regeneration. For this purpose, gases from the sulfide concentrates oxidation reactor (Fig. 1, pos. 1) consisting largely of NO, enter the oxidizing volume (Fig. 1, pos. 3), to which the air is dosed, allowance made for gas mixture analysis, for NO oxidation to N_2O_3 by the reactions:



NO_2 formed as a result of NO oxidation by the air oxygen at a temperature below 140°C has a tendency towards polymerization with formation of N_2O_4 . Accordingly, after NO mixing with oxygen in gas phase, chemical equilibrium of NO, O_2 , NO_2 , N_2O_3 and inert nitrogen of the air will set in.

The equilibrium constant of nitrogen dioxide polymerization

$$2 \text{NO}_2 = \text{N}_2\text{O}_4 + 56.8 \text{ kJ/mol} \quad K_a = \frac{P_{\text{N}_2\text{O}_4}}{P^2 \text{NO}_2}$$

in the range of low concentrations of NO_2 is determined by the formula:

$$\text{Lg } K_a = \frac{2692}{T} + 1.75 \lg T + 0.00484 T - 7.144 \cdot 10^{-6} T^2 + 3.062$$

If concentration C (vol.%) of $\text{NO}_2 > 10\%$, the equilibrium constant is expressed by the following empirical equations:

$$25^\circ\text{C} \quad K_a = 0.1426 - 0.7588 C_{\text{N}_2\text{O}_4}$$

$$35^\circ\text{C} \quad K_a = 0.3183 - 1.591 C_{\text{N}_2\text{O}_4}$$

$$45^\circ\text{C} \quad K_a = 0.6706 - 3.382 C_{\text{N}_2\text{O}_4}$$

where $C_{\text{N}_2\text{O}_4}$ – content of nitrogen oxides in terms of N_2O_4 , mol/liter

$$C_{\text{N}_2\text{O}_4} = \frac{0.5 P_{\text{NO}_2} + 2 P_{\text{N}_2\text{O}_4}}{R \cdot T}$$

where P_{NO_2} and $P_{\text{N}_2\text{O}_4}$ – partial gas pressure, atm.

Rate constant of N_2O_3 formation:

$$\text{NO} + \text{NO}_2 = \text{N}_2\text{O}_3 \quad K_b = \frac{P_{\text{N}_2\text{O}_3}}{P_{\text{NO}} \cdot P_{\text{NO}_2}}$$

is determined by the following empirical equations:

$$25^\circ\text{C} \quad K_b = 2.105 - 45.63 C_{\text{N}_2\text{O}_3}$$

$$35^\circ\text{C} \quad K_b = 3.673 - 78.11 C_{\text{N}_2\text{O}_3}$$

$$45^\circ\text{C} \quad K_b = 6.88 - 196.4 C_{\text{N}_2\text{O}_3}$$

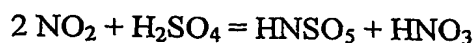
where $C_{N_2O_3}$ – content of NO, NO₂, N₂O₄ in terms of N₂O₃, mol/liter

$$C_{N_2O_3} = 0.5 (P_{NO} + P_{NO_2} + 2P_{N_2O_4}) * \frac{1}{R * T}$$

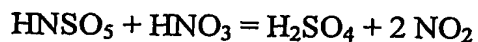
Thermodynamic calculations made for gas mixtures different in composition at various temperatures and pressures proved that it is actually impossible to select conditions permitting formation of solely N₂O₃. The presence of nitrogen oxides like NO₂ and N₂O₄ further gives rise to formation of nitric acid in the oxidation reaction, which is undesirable in the framework of this process.

The process of present invention permits solving the problem:

For separating nitrogen oxides formed in the oxidizer (Fig. 1, pos. 3) from atmospheric nitrogen and other inert gases contained in the gas mixture, nitrogen oxides are absorbed by sulfuric acid solution in the absorber (Fig. 1, pos. 4). During NO₂ nitrogen dioxide absorption by sulfuric acid the following reactions occur:

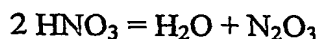
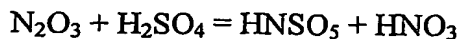


Nitric acid, HNO₃, formed in highly acidic medium of sulfuric acid interacts with HNSO₅ by the reaction:



Hence, absorption of NO₂ and N₂O₄ by sulfuric acid is inefficient, as it results in formation of the initial substances.

Absorption of nitrogen oxides in the form of N₂O₃ by sulfuric acid is very effective, since interaction is complete with formation of HNSO₅:



Thus, nitrogen oxides in the form of N_2O_3 are absorbed completely by sulfuric acid solutions.

NO solubility in sulfuric acid solution is insignificant and at a temperature of 20°C under normal pressure it is:

H_2SO_4 concentration %	100	45	24	0
NO content %	0.0025	0.002	0.005	0.009

The data above suggest that when a mixture of gases consisting of NO , NO_2 , N_2O_3 , N_2O_4 and inert gases is fed to the absorber, solely N_2O_3 will react irreversibly with sulfuric acid. Accordingly, concentration of N_2O_3 will decrease and chemical reactions will take place towards its formation. The rates of gas reactions are very high and equilibrium in the system sets in 0.1-0.5 sec, which permits absorbing nitrogen oxides in the form of N_2O_3 in the absorber in the course of gas residence in it.

3. To decrease the loss of nitrogen oxides with flue gases, stemming from partial pressure of nitrogen oxides above sulfuric acid, nitrous gases absorption will be realized by sulfuric acid, its concentration 75-98%. Advisability of using sulfuric acid solutions with the above-mentioned concentration limits is dictated by the degree of hydrolysis of nitrosyl sulfuric acid, HNSO_5 , in H_2SO_4 solutions, and, accordingly, by pressure of nitrogen oxides over H_2SO_4 surface.

H_2SO_4 concentration %	98	95	92	90	87	80	70	57
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% of HNSO_5 hydrolysis	1.1	4	7.3	12.4	19.4	27.7	49.8	100
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4. Sulfuric acid saturated with nitrous gases enters the denitrator (Fig. 2, pos. 5), where thermal and chemical decomposition of nitrosyl sulfuric acid, HNSO_5 , occurs with formation of the initial acid and nitrous acid, HNO_2 . The decomposition takes place largely as a result of heating, but chemical denitrating agents, like alcohols, formaldehydes and other chemical reducing agents, can also be used for sulfuric acid denitration. High temperature (up to 250°C) and the chemical substances give rise to nitrosyl sulfuric acid and nitrous acid decomposition with evolution of N_2O_3 , which in its turn at this temperature provides equimolar mixture of NO and NO_2 . The gas mixture is fed to the oxidation reactor (Fig. 2, pos. 1), where oxidation of sulfide concentrates stems from the effect of nitrous acid formed upon interaction between nitrous gases and the slurry water.

For saving high-temperature energy media, which are to be used for nitrosyl sulfuric acid heating up to 250°C , copper salt solutions can be used in the process of nitrogen oxides regeneration instead of sulfuric acid. It is a well-known fact that aqueous solutions of monovalent copper salt dissolve readily nitric oxide, NO . In the flowsheet depicted in Fig. 2 waste gases from sulfide ores and concentrates oxidation reactor (Fig. 2, pos. 1) and largely consisting of NO , are absorbed in the absorber (Fig. 2, pos. 4) by monovalent copper salt solution. Chlorides, sulfates, ammonium and other water-soluble salts of monovalent copper can be used as active compounds for nitrogen oxides absorption. Monovalent copper solution saturated with nitric oxide enters the denitrator (Fig. 2, pos. 5), to which from the blower (Fig. 2, pos. 2) compressed air is dosed, possibly with simultaneous heating of the solution. Nitric oxide, NO , is oxidized in dissolved form to N_2O_3 , that is not absorbed by monovalent copper solution and is removed to the oxidizer (Fig. 2, pos. 3). Final correction of the degree of NO oxidation to N_2O_3 form occurs in the oxidizer, after that nitrous gases are fed to the oxidation reactor (Fig. 2, pos. 1).

Denitrated solution of copper salts from the denitrator (Fig. 2, pos. 5) by the pump (Fig. 2, pos. 6) is fed for the absorber (Fig. 2, pos. 4) sprinkling. Neutral nitrogen of the air, which failed to dissolve in the copper salt, is sucked out by the fan (Fig. 2, pos. 7) and is released to the atmosphere. Monovalent copper solutions may contain stabilizers preventing copper oxidation from monovalent to bivalent one, as bivalent copper solutions are not effective solvents of NO. The well-known substances like tributyl phosphate and adipodinitrile, along with other reducing agents, such as formaldehyde, hydrazine, etc., can be used as the stabilizers.

When pure oxygen is used for NO oxidation in regeneration, the hardware block diagram is much simpler, as there is no necessity to remove inert nitrogen of the air from the system. Meanwhile, implementation of a separate regeneration oxidizer (Fig. 2, pos. 3) is an essential element of our new technology, as it permits regeneration by NO converting into N_2O_3 and avoiding nitric acid accumulation in the slurry. Oxygen feeding directly to the oxidation reactor will give rise to parallel formation of nitric and nitrous acids, since the conditions of concentrates oxidation (65-85°C) and conditions of nitric acid regeneration differ in temperature and pressure.

Examples of specific implementation of the method claimed:

1. Copper ore featuring the composition: pyrite – 80%, chalcopyrite – 4%, sphalerite and galenite – 1%, quartz – 7%, chlorite – 2%, sericite – 2%, barite, epidote – up to 1% underwent oxidation according to the hardware block diagram depicted in Fig. 1.

Chemical composition of the ore is: copper – 1.54%, zinc – 0.46%, sulfur – 42.4%, iron – 40.6%, silicon oxide – 9.8%, aluminium oxide – 2.4%, magnesium oxide – 0.42%, calcium oxide – 0.1%, potassium oxide – 0.22%, sodium oxide – 0.12%, gold – 1.4 g/t, silver 13 g/t.

It took 4 hours to realize the oxidation process at the process temperature in the oxidation reactor of 75°C. Turnover of nitric oxide in terms of NO made up 940 grams per kg of the ore in the period of the process conduct. Temperature in the absorber (Fig.1, pos. 4) was maintained at a level of 26°C, temperature in the denitrator (Fig. 1, pos. 5) – at a level of 130°C, ethyl alcohol in the amount of 2 ml per liter of denitrated sulfuric acid solution was used for denitration promotion. Sulfuric acid formed was neutralized by introducing of Ca(OH)_2 into the slurry solution to the level of residual acidity 5 g/l in terms of sulfuric acid. No formation of elementary sulfur was observed as a result of the oxidation process under controlled conditions of the slurry acidity. According to chemical analysis data the content of sulfide sulfur in the cake after the process completion made up 1.6%. Transfer of copper into solution amounted to 98.5% of the initial content in the ore, that of zinc - 97% of the initial content in the ore.

The cake was cyanidated after washing and neutralization. Gold recovery made up 94%, that of silver – 91% of the initial content in the ore.

2. Mixed flotation concentrate of the following composition:

copper – 22.5%, zinc – 3.9%, sulfide sulfur – 40%, iron – 32.6%, silicon oxide – 0.5%, aluminium oxide – 0.4%, lead – 0.18%, organic carbon – 0.22%, gold – 10.6 g/t, silver 71.4 g/t, was subjected to oxidation according to the hardware block diagram depicted in Fig. 2.

Duration of the oxidation process made up 6 hours, at the process temperature in the oxidation reactor 80°C. Turnover of nitrogen oxide in terms of NO amounted to 1670 g/kg of ore during the period of the process. Temperature in the absorber (Fig.1, pos. 4) was maintained at a level of 26°C, temperature in the denitrator (Fig. 1, pos. 5) – at a level of 70°C, formaldehyde in the amount of 0.7 g/liter of solution being used as copper chloride solution stabilizer. Sulfuric acid formed was neutralized by introducing solution of Ca(OH)_2 to the slurry to the level of residual acidity of 3 g/l in terms of sulfuric acid. As a result of the

process conduct with control over the slurry acidity, no formation of elementary sulfur was observed.

According to chemical analysis data the content of sulfide sulfur in the cake after the process completion made up 2.1%. Copper transfer to solution made up 99.1% of the initial content in the ore, that of zinc – 98.3% of the initial content in the ore.

After washing and neutralization the cake was cyanidated. Recovery of gold proved to be 97%, that of silver – 94% of the initial content in the ore.

3. Pyrrhotine ore featuring the following composition:

pyrrhotine – 67.2%, chalcopyrite – 11.1%, pentlandite – 9.5%, magnetite – 5.7%, non-ore minerals – 5.7%, titanomagnetite – 0.2% was oxidized using the hardware block diagram shown in Fig. 3.

Chemical composition:

silicon oxide – 1.6%, aluminium oxide – 1.85%, iron – 52.1%, sulfide sulfur – 30.8%, calcium oxide – 1.03%, magnesium oxide – 0.33%, sodium oxide – 0.17%, potassium oxide – 0.14%, manganese oxide – 0.11%, copper – 3.67%, nickel – 4.2%, cobalt – 1310 g/t, platinum – 1.5 g/t, palladium – 2.2 g/t.

The oxidation process was conducted for 4.4 hours, at the process temperature in the oxidation reactor 75°C. Oxygen consumption for the ore oxidation was 340 g/kg of ore during the process. Sulfuric acid formed was neutralized by introducing solution of $\text{Ca}(\text{OH})_2$ to residual acidity level of 7 g/l in terms of sulfuric acid, 50 g/l NaCl being added to the solution for complexing properties. As the oxidation process was conducted with control over the slurry acidity, no elementary sulfur formation was observed. According to chemical analysis data the content of sulfide sulfur in the cake after the process completion was 1.1%. Copper transfer to solution made up 94.3%, nickel – 96.3%, cobalt – 93.3%, platinum – 91.4%, palladium – 95.2 % of the initial content in the ore.

It follows from the reasoning above that the proposed hydrometallurgical method of sulfide minerals and concentrates processing differs from the known

ones, therefore, the method proposed corresponds to the “novelty” criterion. Comparison of the approach proposed with the Prior Art and other technical approaches in this field of technology permitted identification of signs, which make the proposed approach different from the Prior Art, meanwhile, the differences considered are implicit, which suggests conclusion on compliance of the approach proposed with the “inventive level” criterion. The technical approach has industrial applications.